



The
Patent
Office



U.S.

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

JC542 U.S. PTO

09/533750



03/23/00

#2

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein together with the Statement of inventorship and of right to grant of a Patent (Form 7/77), which was subsequently filed.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 7 March 2000

274499 2455221-1 00031
POL/770 0.01 - 29.0017

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

57.0329 GB NP

2. Patent application number

(The Patent Office will fill in this part)

9907017.9

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Sofitech N.V.

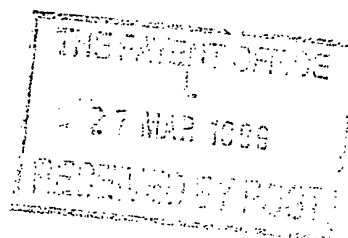
Rue de Stalle 140
B-1180 Brussels
Belgium

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Belgium

6546303005



4. Title of the invention

Additive for Wellbore Fluids

5. Name of your agent (if you have one)

MIRZA, Akram Karim

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

c/o Schlumberger Cambridge Research Ltd
High Cross, Madingley Road
Cambridge
CB3 0EL

Patents ADP number (if you know it)

697 4299001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77


9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form -

Description 8

Claim(s) 1

Abstract 1

Drawing(s) 1 + 1 

10. If you are also filing any of the following, state how many against each item.

Priority documents -

Translations of priority documents -

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77) 1

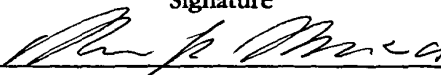
Request for substantive examination (Patents Form 10/77) 1

Any other documents -
(please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date



26 March 1999

12. Name and daytime telephone number of person to contact in the United Kingdom MIRZA, Akram Karim 01223-325268

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Statement of inventorship and of
right to grant of a patent

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

57.0329 GB NP

2. Patent application number
(if you know it)

3. Full name of the or of each applicant

Sofitech N.V.

4. Title of the invention

Additive for Wellbore Fluids

5. State how the applicant(s) derived the right
from the inventor(s) to be granted a patent

The Applicant(s) and the Employer(s) of the Inventor(s) are affiliated Schlumberger companies. The Applicant(s) derived the right to be granted a patent by virtue of agreement with the Employer(s) of the Inventor(s).

6. How many, if any, additional Patents Forms
7/77 are attached to this form?
(see note (c))

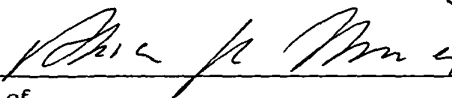
-

7.

I/We believe that the person(s) named over the page (and on any extra copies of this form) is/are the inventor(s) of the invention which the above patent application relates to.

Signature

Date



6 April 1999

8. Name and daytime telephone number of
person to contact in the United Kingdom

MIRZA, Akram Karim

01223-325268

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there are more than three inventors, please write the names and addresses of the other inventors on the back of another Patents Form 7/77 and attach it to this form.
- d) When an application does not declare any priority, or declares priority from an earlier UK application, you must provide enough copies of this form so that the Patent Office can send one to each inventor who is not an applicant.
- e) Once you have filled in the form you must remember to sign and date it.

Patents Form 7/77

Enter the full names, addresses and postcodes of the inventors in the boxes and underline the surnames

LADVA, Hemant Kumar Jethalal
64 Perne Avenue
Cambridge
CB1 3SA
United Kingdom

6471676001

Patents ADP number (if you know it):

SAWDON, Christopher Alan
6 Southview Road
Biscovey
Par
Cornwall
PL24 2HJ
United Kingdom

2698348001

Patents ADP number (if you know it):

HOWARD, Paul Richard
26 Church Street
Great Wilbraham
Cambridge
CB1 5JQ
United Kingdom

76337040001

Patents ADP number (if you know it):

Reminder

Have you signed the form?

- 1 -

Additive for Wellbore Fluids

This invention relates to an additive for wellbore fluids. More specifically, it pertains to an additive for modifying the
5 properties of a filtercake formed at the boundary between wellbore and formation.

BACKGROUND OF THE INVENTION

10

For the production of hydrocarbon wells, boreholes are drilled into subterranean formations. Following standard procedures, a fluid is circulated during drilling from the surface through the interior of the drill string and the annulus between drill
15 string and formation. The drill fluid also referred to as drilling mud is used to lubricate the drill bit. It also balances the formation pressure so as to prevent formation fluids to enter the borehole in an uncontrolled manner.

20 The industry distinguishes between largely three classes of drilling fluids: oil-based, water-based and so-called synthetic muds. Whereas oil-based muds are recognized for their superior qualities for most of the drilling operations themselves, they become increasing undesirable due to their impact on the
25 environment and stricter environmental legislation. Water-based muds are expected to replace oil-based mud as the drilling fluid of choice in major geographical areas.

Other fluid systems used in the oilfield industry are completion
30 and workover fluids. By definition a completion or workover fluid is a fluid that is placed against the producing formation while conducting such operations as well killing, cleaning out, drilling in, plugging back, controlling sand, or perforating. Basic fluid functions are to facilitate movement of treating

- 2 -

fluids to a particular point downhole, to remove solids from the well, and to control formation pressures.

Required fluid properties vary depending on the operation, but
5 the possibility of formation damage is always an important concern. In recent years many new fluid systems have appeared, most due to the recognition of the high risk of reducing the productivity, or completely plugging certain sections of the producing zone, through contact with a foreign fluid.

10

A wellbore fluid typically contains a number of additives. Those additives impart desired properties to the fluid, such as viscosity or density. One class of additives is used as fluid
15 loss agents to prevent the drilling fluid from entering into porous formations.

The basic mechanism of fluid loss control is generally the formation of a filtercake at the interface of the porous or permeable formation layers. As part of the drilling fluid is
20 forced into the formation by the higher pressure within the wellbore, larger particles and additives are left behind and accumulate at the face of the formation. The filtercake thus formed can be regarded as a membrane that protects the formation from further invasion of wellbore fluids. Fluid-loss control
25 agents are selected in view of their quality to form a competent filtercake.

High molecular weight, oil soluble additives have been widely used as diverting agents and in water based drilling and
30 completion fluids. The additives help build an effective filtercake at the formation face and minimize damage. Under flowback conditions, the reservoir hydrocarbons readily dissolve the additive effectively creating holes in the filtercake and aiding formation cleanup. Having a hydrocarbon induced breakdown
35 of the filtercake avoids chemical intervention (clean-up) and

- 3 -

hence can result in a very cost-effective method of drilling wells for hydrocarbon production.

Many different oil soluble additives can be used to control fluid loss. In the application to drilling fluids, high molecular weight thermoplastic hydrocarbon resins are commonly used. United States Patent Nos 3,891,566 and 3,827,498 describes for example a mixture of two oil soluble resins one being friable and the other pliable as fluid loss control agents and as diverting agents. The resin must be used where oil exists and therefore it cannot be used in dry gas wells or in wells with temperature above its softening point. Its high molecular weight and impurities can make it only partially soluble in hydrocarbons causing the residues to damage or block the formation.

It is therefore an object of the present invention to provide a novel class of fluid loss additives that are able to form a competent filtercake while being easily removable from hydrocarbon bearing formations.

SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a low molecular weight, high melting point, crystalline, oil soluble additive for use in wellbore fluids that include drilling, completion, workover, fracturing, acidising, cementing fluids and the like.

The new additive is a wellbore-fluid additive which is preferably a ground crystalline material of melting point over 80°C, preferably over 100°C which is readily soluble in produced hydrocarbons such as crude oil and lighter condensates, and which exhibits a molecular weight of less than 1000, and preferably less than 650.

Its particle size can be adjusted to bridge efficiently across different pore size formations and control its solubility rate. A preferred particle size range is 10000 to 1 micron.

5

Preferred examples of the low molecular weight crystalline additives are 1S-endo-Borneol, camphor or iodine. Other examples include beta carotene with a melting point of 184 degrees Celsius and a molecular weight of 537, lycopene (175; 537),
10 cholesterol (150; 387), lanosterol (139; 426), and agnosterol (165:424).

The invention reduces formation damage, flow initiation pressure, and increases the cleanup efficiency dependent on the
15 formation type. Compared to other additives, the low molecular weight crystalline additive can provide some important advantages. Firstly, the conventional high molecular weight resins, during the initial stages of dissolution in produced hydrocarbons, can be plasticized by the oil to a tacky material.
20 This tends to coalesce to a sticky mass and is very difficult to remove by dissolution. Secondly, the pressure required to start the backflow of oil through such filtercake can be high and therefore the resins have limited use in wells with low drawdown pressures. Thirdly, the level of impurities in the hydrocarbon
25 resin can limit its cleanup. By contrast, the low molecular weight crystalline solids of this invention dissolve smoothly and quickly to give low viscosity solutions.

In a variant of the invention, it is envisaged to reduce the
30 environmental hazards and nuisance caused by some of the new crystalline solids compounds by an encapsulating treatment.

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will
35 become appreciated and understood by those skilled in the art from the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the fluid loss behavior of a drilling fluid dependent on the additive particle size and sequential fluid.

MODE(S) FOR CARRYING OUT THE INVENTION

Using 1S-endo-Borneol ($C_{10}H_{18}O$) having a molecular weight of 154 and melting point of $210^{\circ}C$ ($410^{\circ}F$), it was first bottle tested for its solubility in water, kerosene and kerosene with 5% mesitylene (aromatics) at $25^{\circ}C$. 2 g of the additive added to 50 ml of the test fluid was insoluble in water but dissolved completely, within 5 minutes of mixing in kerosene and kerosene with mesitylene. There was no evidence of any residues in both cases. The additive was insoluble in water at higher temperature of $80^{\circ}C$.

Tests were then performed to demonstrate the ability of this additive to increase the permeability of a drilling fluid filtercake when contacted with kerosene. A 2.5 inch diameter High Pressure-High Temperature filtration cell was used for the tests. Sequential static filtration tests were performed on a filter paper (2 micron pores) at 100 psi pressure and $25^{\circ}C$ temperature using the polymer/carbonate drilling fluid containing 10 ppb of the crystalline additive followed with kerosene. The composition of the drilling fluid is given in Table 1.

Table 1: Composition of a polymer/carbonate drilling fluid.

	lb/bbl	gl ⁻¹
CaCl ₂		

- 6 -

	(74g in 835 ml of H ₂ O)	346	986
	Antifoam	0.2	0.6
5	Starch	6.0	17.1
	Scleroglucan	1.5	4.3
	Biocide	0.1	0.3
10	Calcium carbonate	45.0	128.3

The effect of varying the particle size of the additive (d_{50} of 15 400, 200, and 60 microns) was investigated. Care was taken not to disturb the filtercake when emptying the residual mud from the cell and introducing kerosene.

FIG. 1 shows the fluid loss behavior with elapsed time. After 20 the mud cake build-up period of one hour, the kerosene dissolves the additive in the filtercake and increases its permeability to an extent that is particle size dependent. The strongest effect was observed with approximate particle size of 400 micron. But even 200 micron samples and 60 microns samples resulted in a 25 much increased permeability. In the case of a fine grade the permeability increases by as much as 60 times whereas in the control test without the additive the rate increases by only 6 times. (DISCUSS FIGURE)

30 Filtercake examined at the end of the test showed pinholes distributed uniformly over the entire surface due to the dissolved additive whereas in the control test the pinholes were absent.

35 When water is flowed instead of kerosene through a drilling fluid filtercake containing 60-micron size additive there is no change in permeability, further demonstrating the efficient removal of the additive with kerosene.

40 To illustrate the ability of the present invention to reduce fluid loss, formation damage and initial backflow pressure,

tests were run in a High Pressure - High Temperature cell adapted for cores. The cores were 25.4 mm in diameter and 30 mm in length. Three outcrop cores (Ketton limestone, Clashach sandstone and Birchover sandstone) of widely different permeability and pore size were used. Their permeability was approximately 2400 mdarcy, 850 mdarcy and 10 mdarcy, respectively and median pore size was 60 μ m, 33 μ m and 2 μ m, respectively. The cores were first vacuum saturated in brine (45 gl⁻¹ NaCl and 5 gl⁻¹ CaCl₂) and then flushed with kerosene to residual water saturation. The initial permeability to kerosene was determined from the measured steady state pressure drop across the rock corresponding to the imposed range of constant flowrates (10, 8, 6, 4, and 2 ml min⁻¹). The flowrates used for Birchover was 5 times lower.

Static filtration tests were conducted for 4 hours at 300 psi differential pressure and 25 °C temperature using polymer/calcium carbonate drilling fluid containing 10 ppb of 60 micron additive (in the opposite direction to the kerosene flood). After filtration the cell was depressurised and a backflow of kerosene was imposed at 1 ml min⁻¹ to measure the peak (FIP or flow initiation pressure) and steady state flow pressure. The peak pressure correlates with the rupture of the filtercake. The final permeability was measured using the same procedure as used for the initial permeability. The retained permeability was defined as the ratio of final to initial permeability in percentage.

As shown in Table 2, the additive gave a two-fold increase in the retained permeability and reduced the spurt loss, fluid loss and FIP in the case of large pore size Ketton. The spurt loss was higher compared with the other two rocks of smaller pore size resulting in an internal filter cake. The cleanup of this internal cake was promoted by the presence of the additive resulting in a higher retained permeability and lower FIP. In contrast, an external filter cake was mainly built on the smaller pore size rocks. With little or no internal cake, the

additive contributed little to the retained permeability. However, the external filtercake with the additive was made more easily permeable indicated by a lower FIP by as much as 2 times in the case of Birchover sandstone.

5

TABLE 2

Rock type	Drilling Fluid + / - Additive	Fluid loss at 4 hr g	Initial and final permeability mdarcy	Spurt loss g	Retained Permeability %	FIP psi
Ketton	-	2.4	2619 / 767	0.63	29	5.5
"	-	2.4	4817 / 929	0.78	20	8.0
"	+	1.8	2114 / 1276	0.47	60	3.0
"	+	1.6	2411 / 1647	0.41	68	2.1
Clashach	-	1.4	999 / 572	0.15	77	5.2
"	+	1.2	705 / 540	0.11	77	5.0
Birchover	-	1.5	7.2 / 6.8	0.06	92	76
"	+	1.3	11.7 / 10.2	0.06	87	41

10

For an encapsulating treatment Borneol particles can be ground to an average particle size of 60 microns. Then, the particles can be spray coated using Piccopale 85-55KX oil soluble resin. The resulting coating is nominally 0.1 microns thick. These

15 particles are then added to a typical reservoir water based drilling fluid (composition same as other examples).

CLAIMS

1. A wellbore service fluid to be injected from a surface location through a well tubular into a subterranean formation, said fluid being water based and comprising a particulate additive having the properties of being crystalline, soluble in hydrocarbons and insoluble in an aqueous solution.
2. The wellbore fluid of claim 1, wherein the additives have a molecular weight of less than 1000.
3. The wellbore fluid of claim 1, wherein the additives have a molecular weight of less than 650.
4. The wellbore fluid of claim 1, wherein the additives are prior to use in said wellbore fluid encapsulated.
5. Method of treating a wellbore, including the steps
injecting from the surface a water based wellbore fluid comprising a particulate additive having the properties of being crystalline, soluble in hydrocarbons and insoluble in an aqueous solution;
letting said additive accumulate at the face of a permeable formation;
letting hydrocarbons enter said wellbore through said formation thereby dissolving at least part of said accumulated additive.

ABSTRACT

A low molecular weight, high melting point, crystalline, oil
5 soluble additive for use in wellbore fluids is provided that is
preferably a ground crystalline material of melting point over
80°C, preferably over 100°C which is readily soluble in produced
hydrocarbons such as crude oil and lighter condensates, and
which exhibits a molecular weight of less than 1000, and
10 preferably less than 500, and more preferably less than 300. Its
particle size can be adjusted to bridge efficiently across
different pore size formations and control its solubility rate.

